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DETERMINATION OF TRACE
ELEMENTS IN RUBBER.

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DETERMINATION OF TRACE ELEMENTS

IN RUBBER

ABSTRACT

A procedure utilizing chemical and spectrophotometric methods has been outlined for the determination of aluminum, copper, iron, nickel and silica in unprocessed rubber samples.

The significant results obtained are given in the following table.

Sample	Ash %	Silica %	Insoluble Residue %	Iron %	Aluminum %	Copper %	Nickel %
Natural Rubber	0.32	0.27	<0.0005	0.008	0.013	0.0004	<0.0001
Polysar Krylene	0.112	0.019	<0.0005	0.01	<0.0003	<0.0003	<0.0001
Polysar S.	0.133	0.019	<0.0005	0.006	0.0005	<0.0003	<0.0001
Polysar Krynac	0.312	0.009	0.031	0.0058	0.083	<0.0003	<0.0001
Polysar Butyl	0.37	0.017	0.169	0.0007	0.0023	<0.0003	<0.0001

THE UNIVERSITY OF ALBERTA

THE DETERMINATION OF
TRACE ELEMENTS IN RUBBER

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

FACULTY OF ARTS AND SCIENCE
DEPARTMENT OF CHEMISTRY

by

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MAY 7, 1954.



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ACKNOWLEDGEMENTS

The writer wishes to thank Dr. W.E. Harris, of the Department of Chemistry, for his very helpful advice and criticism, during the course of this study and in connection with the preparation of this manuscript.

The writer also wishes to thank the Physics Department for placing at his disposal the use of spectrographic equipment.

This project was supported in part by a grant from the National Research Council.

TABLE OF CONTENTS

	Page
LIST OF TABLES	i
LIST OF FIGURES	iii
1. INTRODUCTION	1
2. EXPERIMENTAL	
A. DESCRIPTION OF METHODS	5
B. APPARATUS, REAGENTS, And MATERIALS	7
C. SPECTROGRAPHIC ANALYSIS	9
D. INVESTIGATION OF THE METHODS FOR THE DETERMINATION OF THE COMPONENTS	13
E. PROCEDURE USED	
1. Wet Ashing of Rubber	22
2. Concentration of Inorganic Components	22
3. Separation and Determination of Metallic Components	
(a) Separation and Determination of Silica ..	23
(b) Separation of Aluminum and Iron	24
(c) Determination of Iron	25
(d) Determination of Aluminum	26
(e) Separation of Nickel and Copper	28
(f) Determination of Nickel	28
(g) Determination of Copper	29

3.	RESULTS AND DISCUSSION OF RESULTS.	
A.	DETERMINATION OF ASH CONTENT AND SILICA.	30
B.	DETERMINATION OF IRON	32
C.	DETERMINATION OF ALUMINUM	32
D.	DETERMINATION OF NICKEL	36
E.	DETERMINATION OF COPPER	36
4.	SUMMARY OF RESULTS	39
5.	BIBLIOGRAPHY	42

LIST OF TABLES

	Page
TABLE 1. Results of Spectrographic Examination of the Rubber Samples for Metallic Components.	10
TABLE 2. Key to Spectrographic Plates, Figures 1 and 2.	11
TABLE 3. Results of Semi-quantitative Spectrographic Analysis.	12
TABLE 4. Weights of Ash, Silica and Total Insoluble Residue Obtained from Twenty grams of Various Rubber Samples.	31
TABLE 5. Amounts of Iron as Determined from Twenty gram Samples of Rubber. Extraction was made from an Ammonium Tartrate Solution.	33
TABLE 6. Amounts of Iron as Determined from Twenty grams of Rubber. Extraction was made from an Acetate Buffer Solution.	34
TABLE 7. Amounts of Aluminum in Twenty gram Samples of Rubber. Extraction was made from an Acetate Buffer Solution.	35
TABLE 8. Amounts of Nickel in Twenty gram Samples of Rubber.	37

TABLE 9. Amounts of Copper in Twenty gram
Samples of Rubber 38

TABLE 10. Summary of the Analyses of the Inorganic
Components in the Various Rubber
Samples 40

TABLE 11 The Average Values for the Analyses of
the Various Rubber Samples. 41

LIST OF FIGURES

	Page.
FIGURE 1.	Apparatus for the Wet Ashing Procedure..... 7
FIGURE 2.	Spectra of the Ashed Products of the Rubber Samples Containing a Base Matrix of Indium Oxide and Carbon Dust. Spectra of Known Metal Salts. 11A
FIGURE 3.	Spectra of the Ashed Products of the Rubber Samples and of Known Metal Salts. 11A
FIGURE 4.	Absorption Curves for the 8-quinclinate Complexes of Aluminum and Iron in Chloroform, from an Ammonium Tartrate Solution. 14
FIGURE 5.	Absorption Curves of Chloroform Solutions of Iron and Aluminum 8-quinolates, from an Acetate Solution. 15
FIGURE 6.	Absorption Curves, Aqueous Nickelic Dimethyl Glyoxime, Copper 8-quinolinate in Chloroform. 16
FIGURE 7.	Standard Curves for Iron and Aluminum Quinolates in Chloroform, at Specified Wavelengths. 19
FIGURE 8.	Standard Curve for Nickelic Dimethyl Glyoxime at 460 millimicrons. 20
FIGURE 9.	Standard Curve for Copper 8-quinolinate in Chloroform at 410 millimicrons. 21

1. INTRODUCTION

A greater understanding of the importance of the presence of minute or trace amounts of impurities in crude or refined products is being achieved at present, the properties of materials often being influenced to a great extent by their presence. For instance, in silver small quantities of such impurities as bismuth and copper affect the reproducing qualities of a photographic plate, when the silver is used for this purpose. Again it is well known that minute differences in soil minerals profoundly influence plant growth and development, while vanadium, iron, and nickel in small amounts interfere with the catalytic cracking of oil (9).

Similarly, in rubber traces of metals may or may not be harmful. Rabald (16) states that ferrous iron is harmful to GR-S, and that copper will accelerate the aging of Neoprene. Other polymers like Butyl, which are nearly saturated, are unaffected by large amounts of any metal or its salt. Some metals may catalyze excessive oxygen absorption of the raw and vulcanized rubbers, which results in a scission of polymer chains. This can be considered as an accelerated aging process. The subject of aging and the part played by traces of metals is, however, too extensive to be discussed here (16).

With the development of instruments such as the spectrograph, spectrophotometer, and polarograph, the determination of trace amounts of impurities in materials has been greatly facilitated. In addition, organic compounds that produce selective

reactions with metals have been developed, which especially have aided work with the spectrophotometer and colorimeter. Sandell (18), has compiled an extensive list of reagents and methods for the determination of traces of metals, but this work is still far from being completely satisfactory. With these aids, trace element analysis has been carried out on a wide variety of materials.

Often the major problem of a chemical analysis is the separation of the components in a form which provides for their easy determination. When one is examining a material that cannot be brought into solution, the analytical problem is more difficult. However, often the solubility problem can be circumvented by the use of a spectrograph. With this instrument it is possible to analyse complex mixtures.

The spectrograph has been used by such workers as Milner (12), Gunn and Powers (4), Key and Hoggan (10), and Meeker and Pommatti (11), in the determination of trace elements in oil. The latter two groups utilized a direct spectrographic analysis of the oil without ashing of the sample. Again, it is of interest to note that Mitteldorf and Landon (13) spectrographically determined the quantities together with the quality of meat, the beef being dry ashed first to obtain a sample suitable for spectrographic analysis. Heggen and Strock (7) have also studied a wide variety of materials from tree leaves to crude oils. They have utilized both dry ashing and wet ashing techniques to prepare samples. Their use of a mixture of 8-quinolinol, thionalide, and tannic acid for concentration purposes is of particular interest. With rubber, however, direct analysis by spectrographic means is nearly impossible. First, the

high carbon content of the compound produces interfering cyanogen lines, and secondly, the material is very difficult to handle in the electric arc. Also, unfortunately, spectrographic equipment is not always readily available, thus making desirable methods involving more common and less costly instruments.

Dry or wet ashing of the organic material is often used as a method of removing the carbon from the material. In the dry ashing process, the material either can be ignited directly, as is done with oil samples (4), or heated slowly in the presence of air (12,13). Morgan and Turner (15) demonstrated that insignificant amounts of metallic oxides were lost with the dry ashing of oil samples. This necessitated carefully controlled combustion with a final ignition at less than 500°C .

A strong oxidizing acid is necessary in a wet ashing process. The use of perchloric acid was first introduced here by Kahane, for the determination of sulphur in rubber samples (8). Again, Hamlin (5) describes acid ashing techniques on fabrics with particular reference to the use of perchloric acid, outlining the optimum acid concentrations necessary and the time required for complete oxidation. The most common acid used, however, is sulphuric acid, the sample being generally evaporated to the oxidizing fumes of sulphur trioxide.

Prior to the last few years, analysts of rubber-like materials have been concerned mainly with the finished rubber products. The American Society for Testing Materials (1) outlines techniques for the determination of a wide variety of metals and organic

constituents in processed rubber. E vidently only copper and manganese have been determined in crude rubber. Recently, Bekkedahl (2), of the United States Bureau of Standards, has summarized the important developments in connection with the analyzing of rubber. His review indicated that intensive investigations have been undertaken to derive newer and faster methods for the chemical analysis of this material, methods for the analysis of traces of metals such as cadium, copper, magnesium and zinc having been reported.

With these things in mind, an investigation was undertaken to determine the amounts of inorganic material present in various types of crude rubber, our objective, being the development of methods suitable for routine analysis.

2. EXPERIMENTAL

A. DESCRIPTION OF METHODS

The experimental work of this thesis can be divided into two sections:

1. Destruction of the rubber and concentration of the inorganic components.
2. Separation and determination of inorganic components.

A preliminary investigation by direct spectrographic analysis of the rubber samples was attempted, but was unsuccessful. The intense cyanogen lines produced masked any possible elemental lines, and the sample itself was difficult to handle. Tuning considerably at the arcing temperature, the samples produced a self absorbing medium for the excited atoms.

A wet ashing procedure utilizing perchloric acid (8) was then used and was successful on samples weighing as much as ten grams. When an attempt to ash a twenty gram sample of Butyl rubber was made, an explosion occurred. The force of this explosion was sufficient to blast a hole six inches in diameter through the floor of the fume cabinet, a floor composed of three-eighths inch tile, supported by two inch wood planking and a cement reinforced copper screen. Descriptions of similar explosions involving anhydrous perchloric acid when used with organic materials have been reported (6). Thus, though perchloric acid is very effective in removing carbon, it was decided to discontinue its use because of its unpredictability.

Dry ashing at controlled low temperatures was next tried, but

was found to be ineffective. With rubber samples of five grams, uncontrollable foaming and fuming occurred. It is believed that some of the inorganic components are lost with the dense fumes by mechanical entrainment. Dry ashing was then tried in a closed vessel, and the fumes were led through an acid trap. When this was done an oily solution collected in the acid trap, indicating that the rubber had not been completely oxidized. Since incomplete oxidation was achieved, inorganic components again could be lost.

The wet ashing method adopted consisted of using hydrochloric, nitric and sulphuric acids, and evaporating the material to fumes of sulphur trioxide. The reaction of nitric acid with rubber is highly exothermic. Therefore, to prevent destruction of cork or rubber joints, ground glass equipment was used. This process was incomplete as far as complete removal of carbon was concerned, but was adequate in that it completely charred the material. The precipitation procedure of Heggen and Strock (7) then was used to recover the metallic components that were in solution. After removal of colloidal carbon by filtration, the residue was ignited to 450°C in an electric furnace, thus bringing about the removal of the excess carbon without loss of the inorganic material (7). The resulting ash was then subjected to chemical or spectrographic analysis.

B. APPARATUS, REAGENTS and MATERIALS

All spectrophotometric measurements were carried out with a Beckman Model DU Spectrophotometer. The pH measurements were made with a Beckman Model H2 pH meter. The apparatus used in the wet ashing procedure consisted of a one thousand millilitre ground glass Erlenmeyer flask fitted with a ground glass Allihn condenser, (Fig.1) the condenser being used to minimize losses of volatile inorganic components. (17).

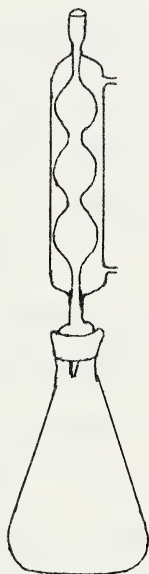


FIG.1

Apparatus for the wet ashing procedure.

All acids used were of C.P. quality. The water used was redistilled through a block tin condenser. Pure ammonium hydroxide was obtained by heating C.P. ammonium hydroxide, and absorbing the

ammonia in water. The reagent 8-quinolinol was purified by recrystallization from dilute ethanol. All other reagents used were of Reagent quality. Aqueous solutions were obtained by dissolving the necessary amount of reagent in the redistilled water. Ammonium acetate and the purified ammonium hydroxide solutions were stored in paraffin lined bottles. Reagent quality chloroform was purified by treating it with concentrated sulphuric acid and water, and then drying the chloroform over calcium chloride. After drying for twenty four hours, the dried chloroform solution was distilled.

The materials investigated were supplied by the Polymer Corporation, Sarnia, Ontario and were as follows:

1. Rolled natural rubber. This is a polyisoprene.
2. Polysar S*. This is a butadiene styrene copolymer, polymerized at 50°C .
3. Polysar Krylene*. This is of the same composition as Polysar S but is polymerized at 5°C .
4. Polysar Krynac*. A polymer of butadiene and acrylonitrile polymerized at 5°C .
5. Polysar Butyl*. This is polyisobutylene, polymerized at minus 80°C .

* Registered Trade Mark.

C. SPECTROGRAPHIC ANALYSIS

The ash of each of the five rubber samples was analysed spectrographically by the arc excitation method. Pure carbon electrodes were used, and the resulting spectrum was recorded on a Kodak 33 photographic plate (Fig.3). Solutions of pure metal salts were dried in carbon electrode holders and their spectra were also recorded.

Samples of ashed rubber were prepared according to the procedure of Heggen and Strock (7). They used indium oxide and carbon dust as a base matrix, so that the sample mixture was composed of 12.1% indium oxide and approximately 67% carbon dust. These samples then were excited, using the arc excitation method (Fig.2). Spectra of metal salts without base matrix were also recorded.

Visual comparison was made of these two figures to identify the constituents present. Unfortunately, no spectrum of the base matrix was obtained. Therefore, the amount of impurities from this source could not be determined. The elements identified by examination of figures 2 and 3 are tabulated in Table 1.

A semi-quantitative analysis of the samples containing the base matrix was also obtained from a private source. The results of this examination are tabulated in Table 3.

It appears therefore that the principal inorganic materials which are present are:

aluminum, calcium, copper, iron, magnesium, nickel and silica.

The spectrographic results were used as guides in the analytical procedure.

Table 1. Results of Spectrographic Examination of the Rubber Samples for Metallic Components from figures 1 and 2.

Element	Natural Rubber.	Polysar S.	Polysar Krylene.	Polysar Krynac.	Polysar Butyl.
Aluminum	2	2	1	5	1
Barium	1	1	1	1	1
Copper	4	1	5	2	3
Iron	1	1	1	1	1
Magnesium	5	6	5	3	1
Nickel	1	1	1	1	1
Silver	1	1	1	1	1
* Xa	1		1		1
* Xb	1		1		1

The numbers presented above are a measure of the relative intensities of the spectrum lines, the least intense being represented by the number 1.

The base matrix for the figures in Table 3, is the carbon of the electrodes when metal ores are being analysed. Since the base matrix for the rubber samples is different, it is likely that the reported values of some of the elements are high. In some cases metals reported in Table 3 are probably not present in other than the carbon electrodes.

* These are two spectrum lines which were not identified.

Table 2. Key to Spectrographic Plates, Figures 1 and 2.

Figure 2	Spectrum Number	Figure 3
Blank, carbon	1	Blank, carbon
Nickel	2	Calcium
Aluminum	3	Antimony
Manganese	4	Tin
Magnesium	5	Magnesium
Copper	6	Silver
Iron	7	Cobalt
Indium Oxide	8	Nickel
Polysar S. (no matrix)	9	Copper
Polysar Krylene (no matrix)	10	Barium
Polysar Butyl (matrix)	11	Aluminum
Polysar Butyl (matrix)	12	Iron
Polysar Krynac (matrix)	13	Polysar Butyl (matrix)
Polysar Krynac (matrix)	14	Polysar Krynac (matrix)
Polysar Krylene (matrix)	15	Polysar Krylene (matrix)
Polysar Krylene (matrix)	16	Polysar S. (matrix)
Polysar S. (matrix)	17	Natural rubber (matrix)
Polysar S. (matrix)	18	Polysar Butyl (no matrix)
Natural rubber (matrix)	19	Polysar S. (no matrix)
Natural rubber (matrix)	20	Polysar Krynac (no matrix)
Blank, carbon	21	Polysar Krylene (no matrix)
	22	Natural rubber (no matrix)
	23	Blank, carbon (no matrix)

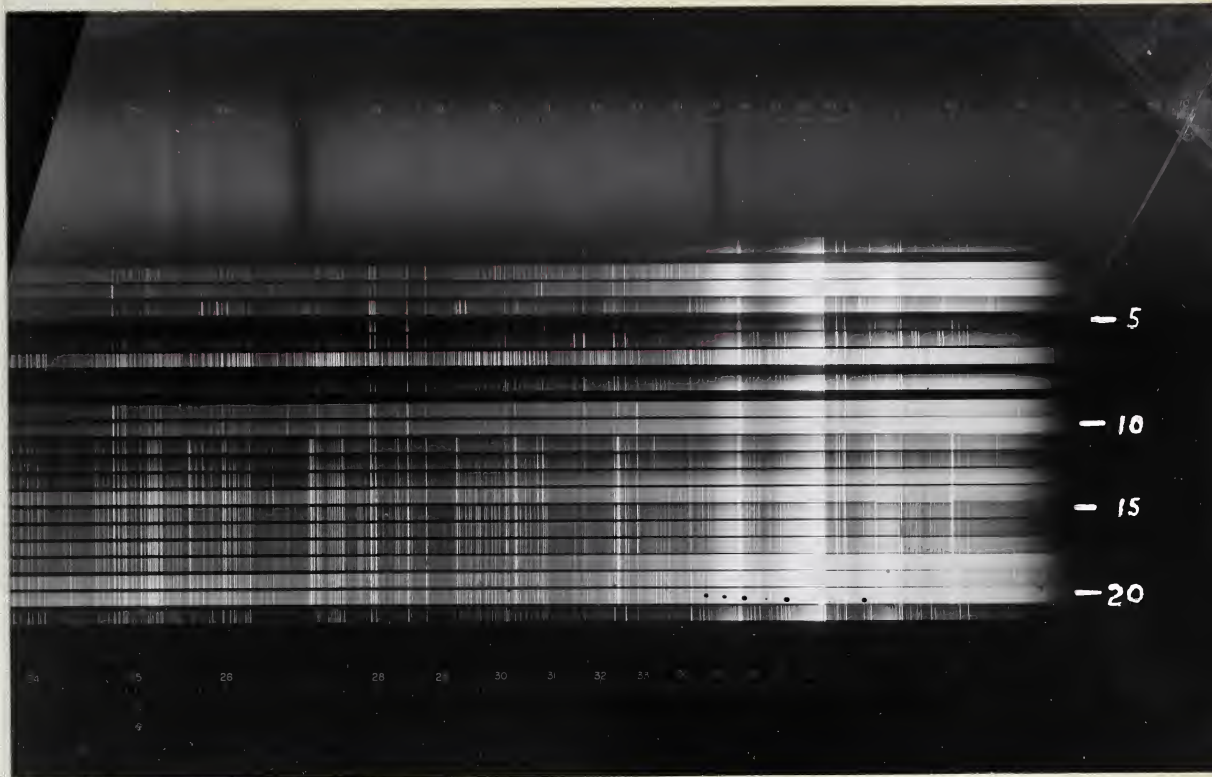


FIGURE 2.

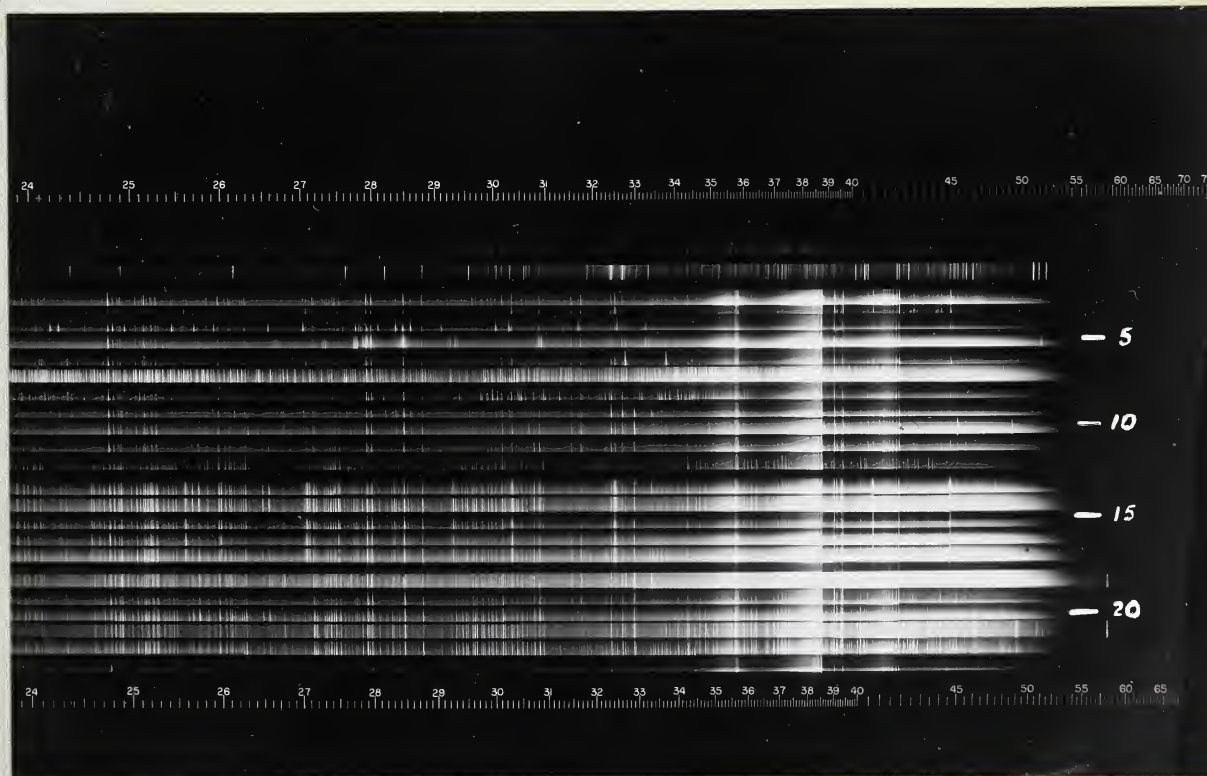


FIGURE 3.

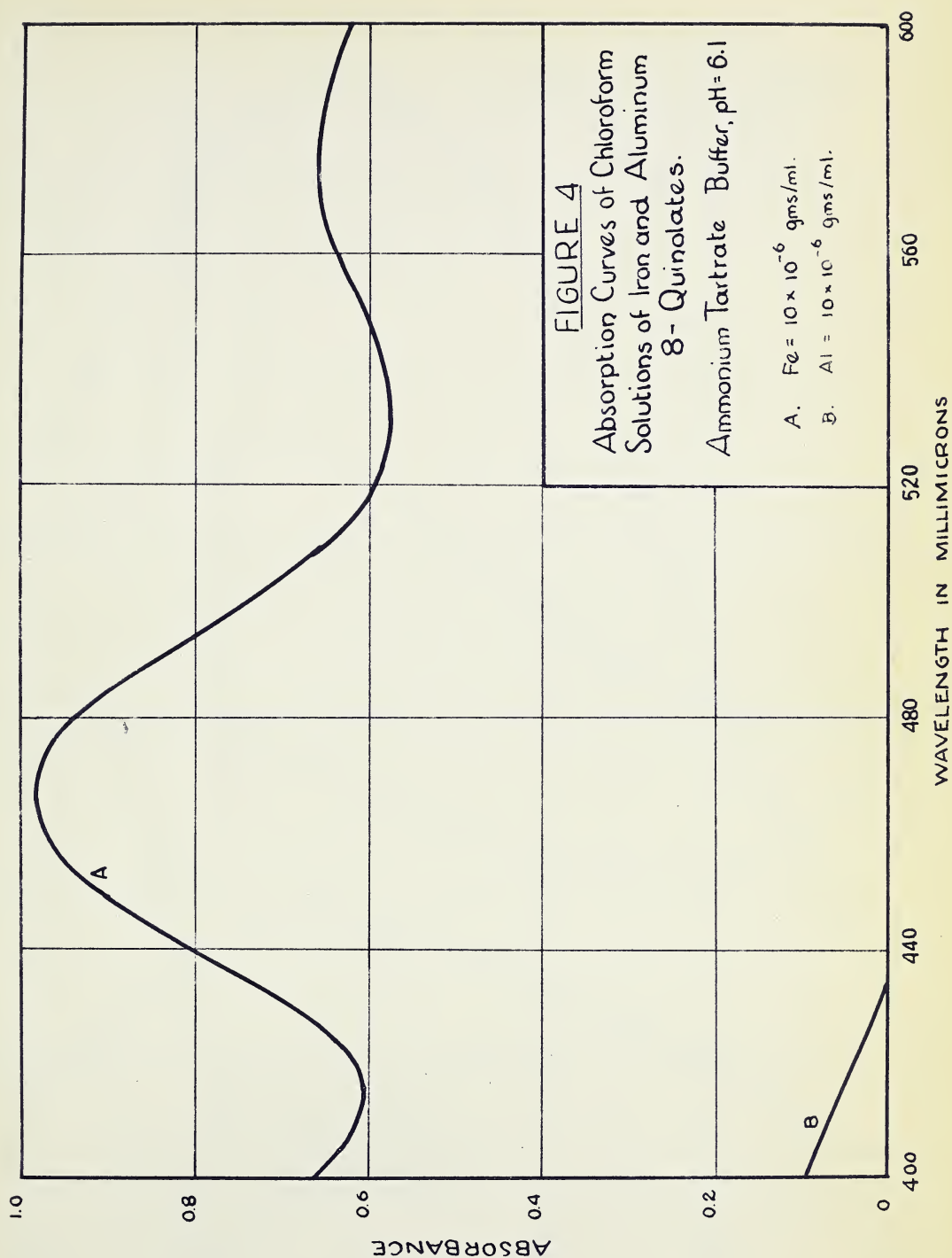
Table 3. Results of Semi-quantitative Spectrographic Analysis

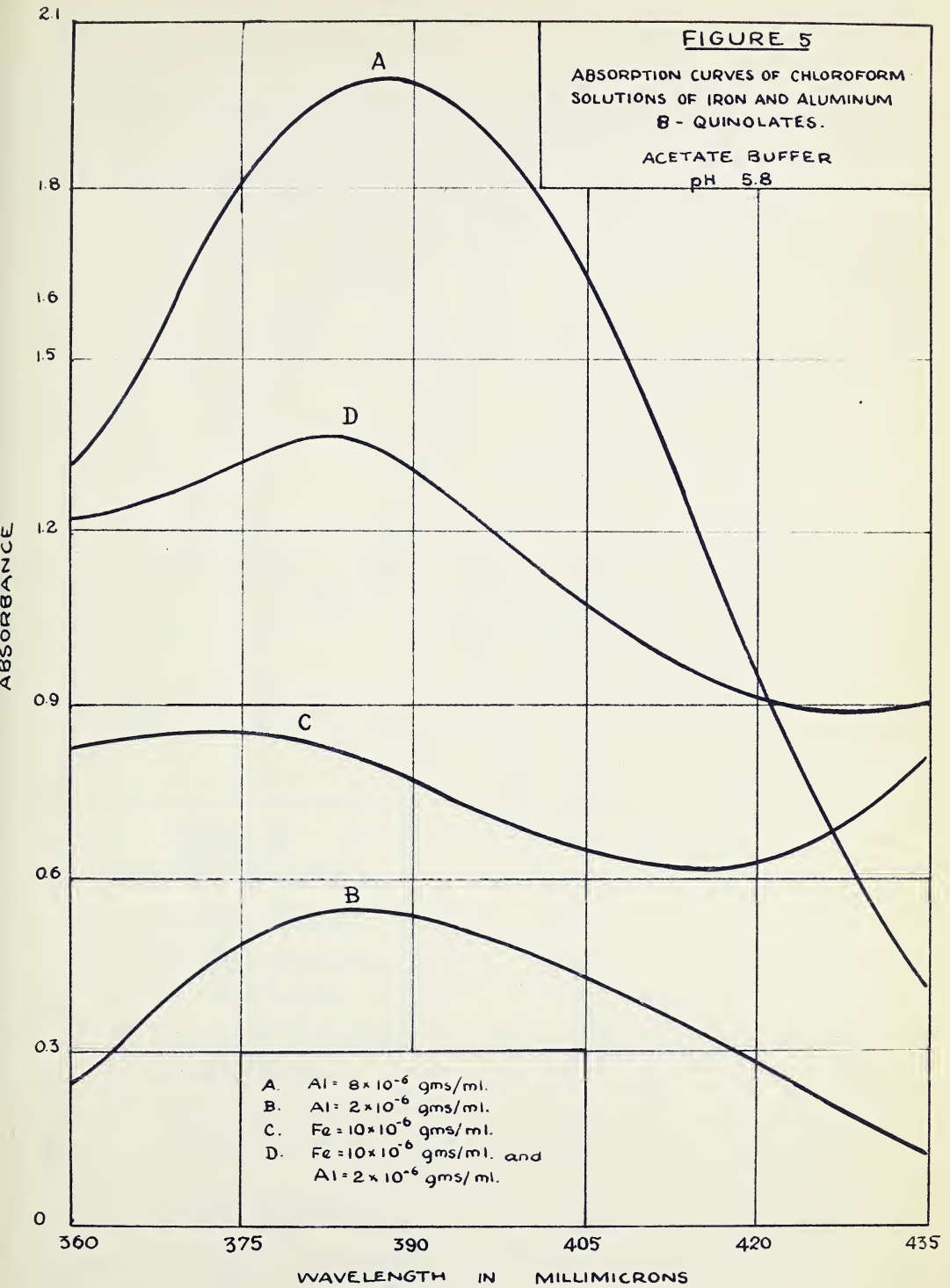
Element	Sensitivity Carbon Base %	Natural Rubber %	Polysar S. %	Polysar Krylene %	Polysar Krynac %	Polysar Butyl %
Aluminum	0.002	2.	0.5	0.5	5.0	5.
Barium	0.01	0.2	0.1	<0.1	<0.1	0.1
Bismuth	0.002	<0.1	<0.1	<0.1	<0.1	<0.1
Boron	0.002	0.1	0.1			
Calcium	0.0004	0.1	0.2	0.1	<0.1	0.1
Chromium	0.001	<0.1	<0.1	<0.1	<0.1	<0.1
Copper	0.0002	<0.1	<0.1	<0.1	<0.1	<0.1
Iron	0.003	0.5	0.5	1.0	0.5	0.5
Lead	0.015	0.5	0.5	0.5	0.5	0.5
Magnesium	0.0004	0.3	0.5	1.0	0.2	0.2
Molybdenum	0.002	<0.01	<0.01	<0.01	<0.01	<0.01
Nickel	0.002	<0.1	<0.1	<0.1	<0.1	0.1
Phosphorous	0.12	0.5				
Silica	0.002	10.	2.	2.	1.	1.
Silver	0.002	<0.004	<0.004	<0.004	<0.004	<0.004
Sodium	0.15	0.5	1.	1.	0.5	
Tin	0.007	<0.1	<0.1	0.1	0.1	<0.1
Titanium	0.002	0.2	<0.1	0.1	<0.1	0.1
Zinc	0.02	<0.1	<0.1	<0.1	<0.1	1.
Weight Sample Grams		0.2214	0.1467	0.1947	0.3729	0.2613

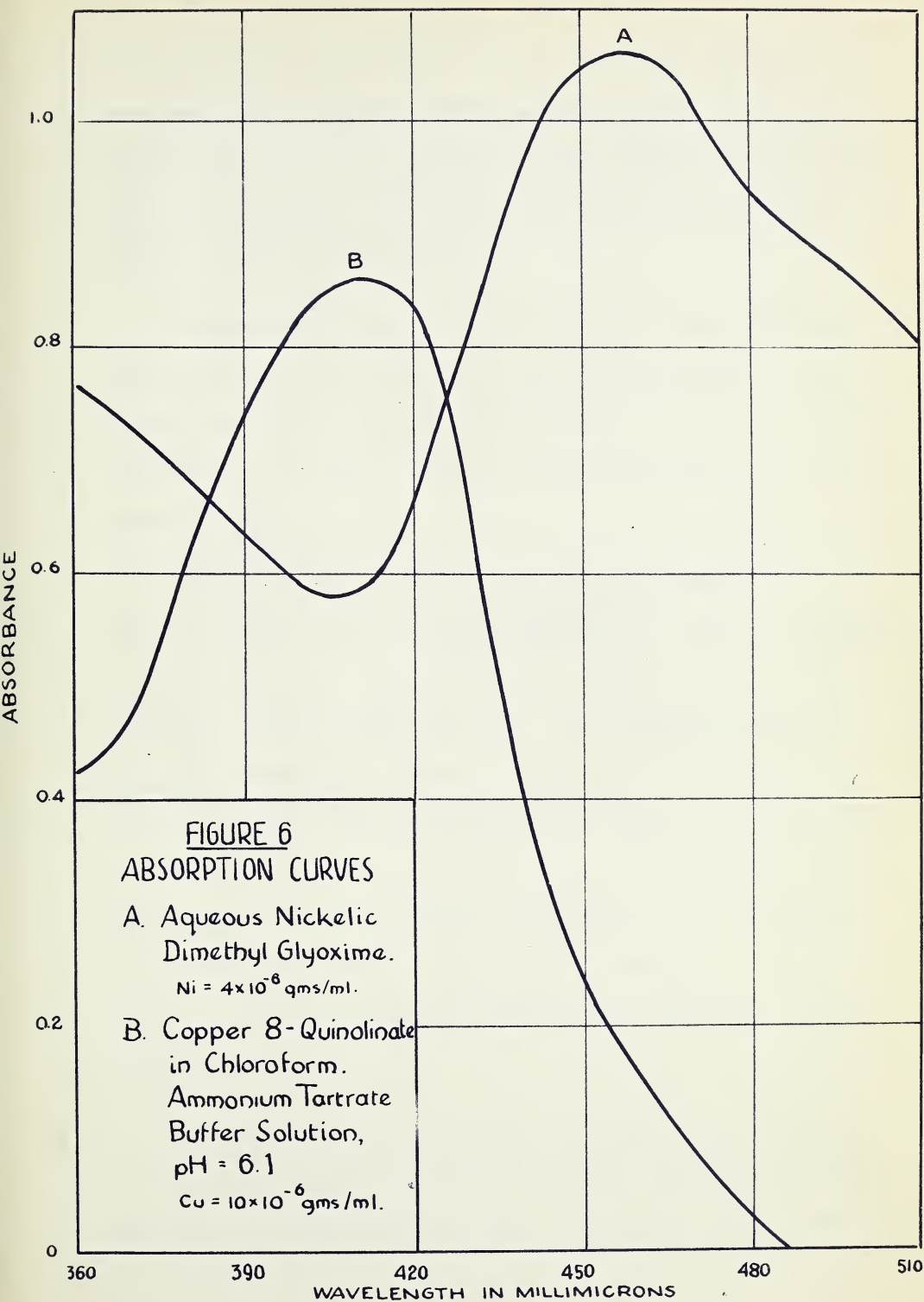
D. INVESTIGATIONS OF THE METHODS FOR THE DETERMINATION OF
THE COMPONENTS.

Moeller (14) investigated the suitability of a 0.01% solution of 8-quinolinol in chloroform for the spectrophotometric determination of iron, aluminum and copper. Gentry and Sherrington (3) used a 1.0% solution of 8-quinolinol in chloroform and found it to be more effective in that complete extraction of the metal complexes were possible over a wider pH range. Their method, with modifications, was the one used in this thesis for the determination of aluminum, iron, and copper.

Moeller also states that it is possible to co-determine iron and aluminum as quinolate complexes in chloroform. It was found that the concentration of the aluminum should not be greater than four times the concentration of the iron when a sodium acetate buffer solution is used. Since one cannot be sure that the relative concentrations of aluminum and iron are always in the proper proportions, it was decided to determine these separately. Iron therefore was determined in a tartrate buffered solution. The absorption curves for these iron and aluminum quinolate complexes are shown in figures 4 and 5. It can be seen from these figures that iron shows an appreciable absorption in the range of the aluminum absorption (Fig.5). However, the absorption of iron at 387.5 millimicrons follows Beers' Law (Fig.7). The absorbance of mixed known solutions of iron and aluminum were found to be additive (curve D, Fig.5). For the absorption curve aluminum quinolate shows a maximum at 387.5 millimicrons (Fig.5). Beers' Law was found to hold-up to concentrations of 8×10^{-6} grams of aluminum







per millilitre, (Fig.7) which is close to the upper limit of measurement with the Beckmann DU spectrophotometer. Since this limit is low, only small aliquots of sample solution are required. In a tartrate buffer, the aluminum complex is not extracted as easily as from an acetate solution.

The absorption curve for iron quinolinate shows an absorption maximum at 470 millimicrons, and a broader maximum at 570 millimicrons (Fig.4). Beers' Law was found to hold up to concentrations of 10×10^{-6} grams of iron per millimetre for both maxima (Fig.7).

Nickel and copper both form complex quinolates. In a solution of chloroform, the nickel complex has a maximum absorbance at 395 millimicrons, whereas the copper complex has a maximum absorbance at 410 millimicrons (14). In a slightly ammoniacal solution, nickel can be separated from copper by a chloroform extraction of the nickel-dimethyl glyoxime complex (19). The amount of the nickelic-dimethyl glyoxime complex can be determined spectrophotometrically. This complex forms a well defined maximum at 460 millimicrons (Fig.6). Copper can be determined by forming the copper quinolinate complex and measuring its absorbance in chloroform (Fig.6).

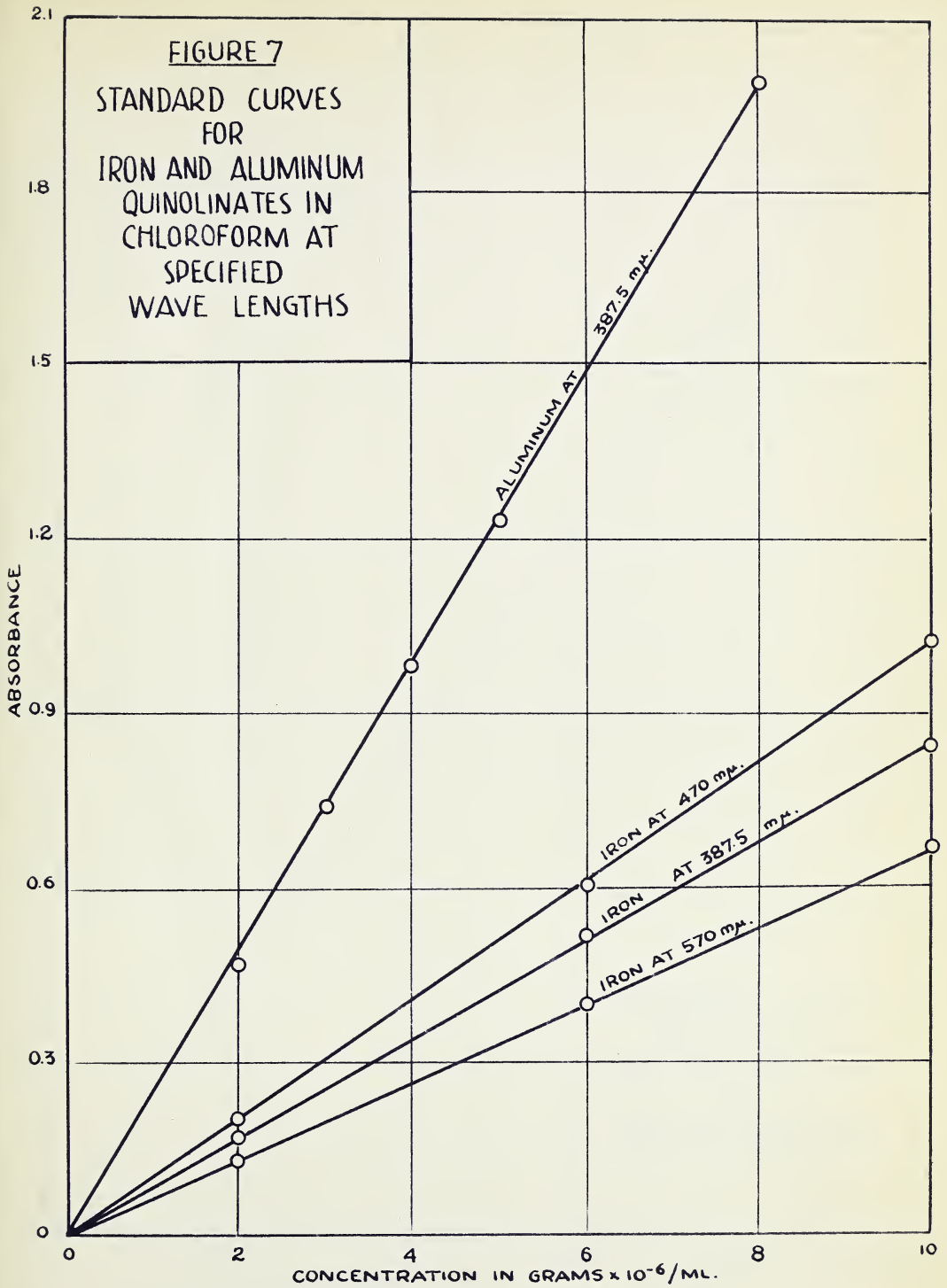
In contrast to the very stable metal quinolinate complexes in chloroform, the aqueous nickelic dimethyl glyoxime complex is not stable for long periods of time. A series of tests showed that

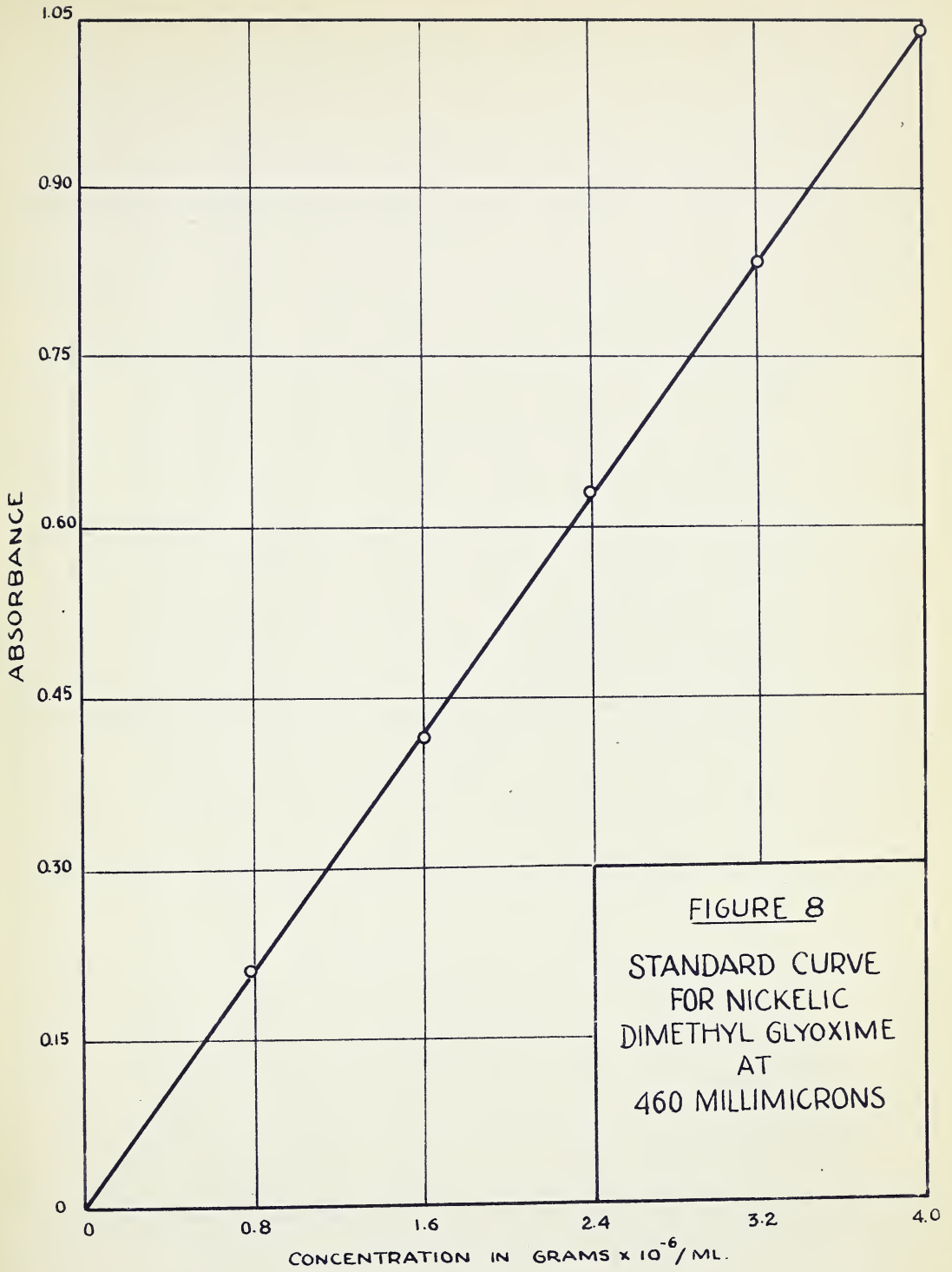
ten minutes after mixing, the absorbance was constant for a period of only about five minutes. The absorbance then increased in value.

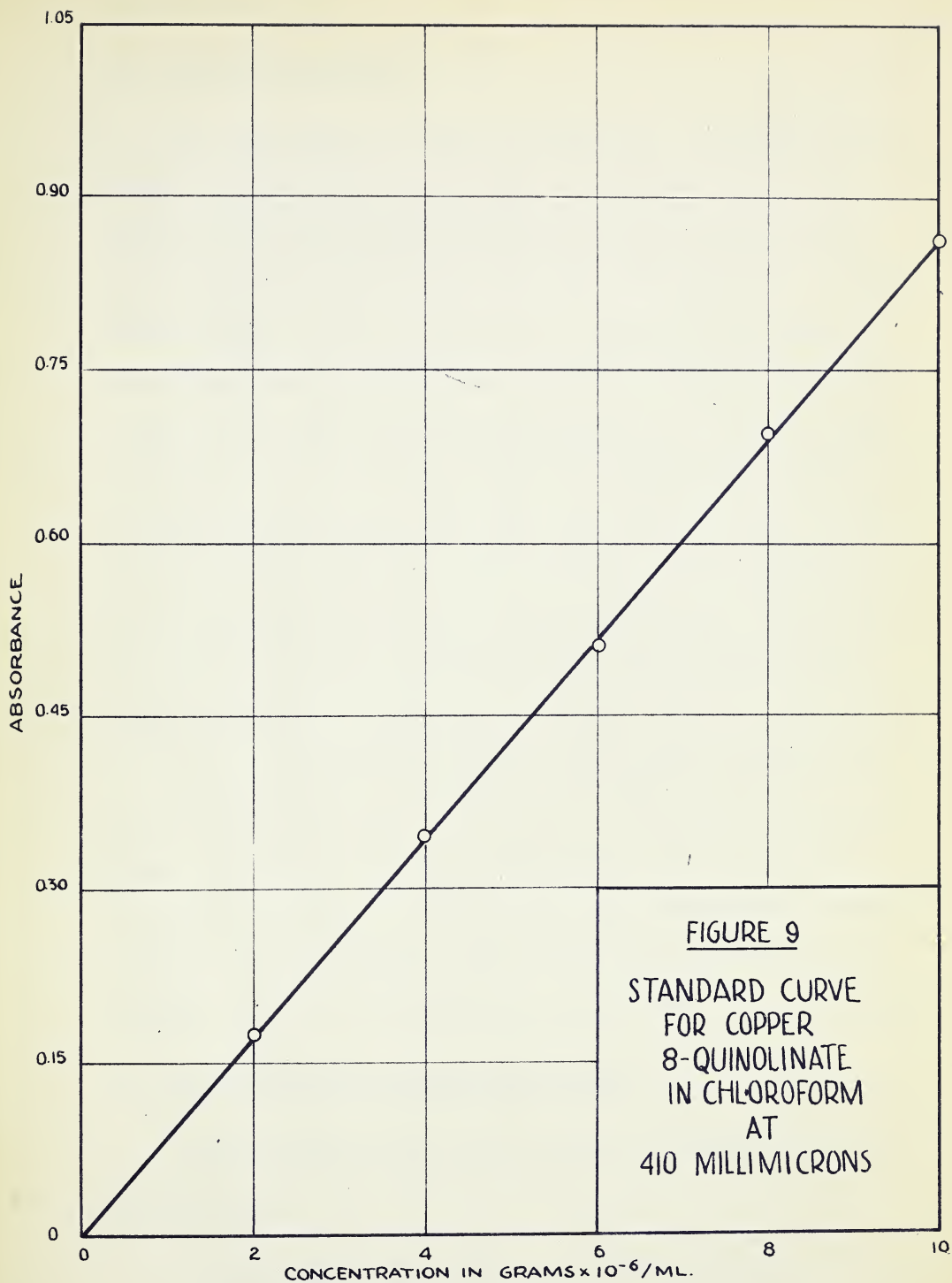
Standard curves were prepared by determining the absorbance of known metal solutions. These solutions were treated in the same way as were the sample solutions. The liquid in the reference cell in the 8-quinolinol chloroform series of absorbance measurements was of the same composition as the extraction solution. In the determination of nickel the reference cell was filled with distilled water.

Beers' Law was found to hold for the nickel and copper up to concentrations of 10×10^{-6} grams of metal per millilitre.

FIGURE 7
STANDARD CURVES
FOR
IRON AND ALUMINUM
QUINOLINATES IN
CHLOROFORM AT
SPECIFIED
WAVE LENGTHS







E. PROCEDURES USED

1. Wet Ashing of Rubber

A 20 gm. sample of rubber was placed in a 1000 ml. ground glass flask. An Allihn water condenser was then fitted to the neck of this flask (Fig.1). One hundred mls. of concentrated nitric acid were added through the neck of the condenser, and the mixture gently heated on a hot plate. During the nitration of the rubber, considerable heat was evolved. The hydrochloric acid tended to slow this reaction and prevented loss of sample. After refluxing for one half hour to expel nitrogen dioxide, 25 mls. of concentrated hydrochloric acid were added and the mixture refluxed for an additional half hour. The condenser was then converted to an air condenser by detaching the water connections. Twenty-five mls. of concentrated sulphuric acid were added and the mixture slowly evaporated to dense fumes of sulphur trioxide. After cooling, water was again passed through the condenser and 25 mls. of dilute hydrochloric acid and 100 mls. of redistilled water were added. The mixture was again refluxed for a half hour, with intermittent shaking to break up the larger agglomerates of charred carbon. Nitrosyl sulphuric acid was also decomposed by the refluxing. After this the mixture was transferred to an 800 ml. beaker.

2. Concentration of Inorganic Components.

The following is the method of Heggen and Strock (7) with modifications.

To the solution from the ashing process was added 10 mls. of

5% 8-quinolinol in 2 N acetic acid . Ammonium hydroxide was added to this with stirring until a pH of 1.8 was reached. Then 30 mls. of 3 M ammonium acetate were added, with 2 mls. of 10% tannic acid in 3 M ammonium acetate, and 2 mls. of 1% thionalide in glacial acetic acid. After adjusting the pH to 5.2* with ammonium hydroxide, the mixture was allowed to settle overnight.

The mixture was then filtered with the aid of a water pump. The precipitate was transferred to a previously ignited porcelain crucible and placed in a cold muffle furnace, the temperature of which was gradually increased over a period of six hours to 450°C. This temperature was maintained for a period of six hours. The residue was then ignited over a Bunsen burner for twenty minutes to remove any remaining carbon. After cooling in a dessicator, the ash was weighed.

3. Separation and Determination of Metallic components.

(a) Separation and Determination of Silica.

To the dry ashed residue from the precipitation procedure above was added 10 drops of concentrated hydrochloric acid. After digestion

* The final pH of 5.2 is critical, for at this pH or lower the calcium and magnesium quinolinates do not precipitate, even with relatively high concentrations of calcium and magnesium. A higher pH should be permissible when the materials being examined are low in these elements. If the pH is lower than 5.2, there will be incomplete precipitation of chromium, nickel, lead and tin.

on a hot plate for fifteen minutes, 30 drops of 60% perchloric acid were added. The material then was evaporated slowly to fumes of perchloric acid, and then acid treatment was repeated. After cooling, 5 mls. of distilled water were added, and the material brought to a boil. It then was filtered through a quantitative filter paper and the precipitate washed five times with 2 mls. portions of hot water. The residue was ignited in a previously ignited and weighed platinum crucible, and the amount determined by weighing (Table 4). To this residue was added 5 drops of concentrated sulphuric acid and 1 ml. of hydrofluoric acid. After evaporation of the residue to fumes of sulphur trioxide, the acid treatment was repeated. The material then was evaporated to dryness, and ignited for a period of fifteen minutes. Its weight was determined after cooling to room temperature in a dessicator. The loss in weight due to the hydrofluoric acid treatment was assumed to be silica.

To this last residue was then added 5 drops of concentrated hydrochloric acid, and 20 drops of water. After bringing the solution to a boil, it was filtered and the filtrate combined with the filtrate obtained in the preceding paragraph. The residue then was ignited, and its weight determined. This "insoluble" residue was retained.

(b) Separation of Aluminum and Iron

The perchloric acid filtrate from the previous section was warmed, and concentrated ammonium hydroxide added dropwise until the

solution smelled faintly ammoniacal. After digestion for half an hour at low temperature, the ferric hydroxide and aluminum hydroxide were filtered. The hydroxide precipitate then was washed five times with cold 0.1 N ammonium hydroxide and cold water. Receivers then were changed. The ferric and aluminum hydroxides were dissolved by washing with 2 ml. portions of hot dilute hydrochloric acid and finally with hot water.

The residue on the filter paper was ignited and weighed, then combined with the "insoluble" residue from the preceding section. This combined material was called the "total insoluble residue."

The hydrochloric acid filtrate was almost neutralized with ammonium hydroxide, and the solution diluted to 100 mls. with distilled water. The iron and aluminum were determined spectrophotometrically on aliquots using 8-quinolinol and chloroform.

(c) Determination of Iron

The extraction method of Gentry and Sherrington (3) was followed.

An aliquot of the iron and aluminum containing solutions was added to 25 mls. of a 4% ammonium tartrate solution of pH equal to 6.1, in a separatory funnel. The aliquot was of sufficient volume to produce a concentration of approximately 50×10^{-6} grams of iron per millilitre. To this mixture was then added 4.5 mls. of 1% 8-quinolinol in chloroform solution. The mixture was shaken for one

minute and the chloroform extract transferred to a 10 ml. volumetric flask. The extraction process was repeated with another 4.5 ml. portion of the chloroform solution. The extracts were then diluted to volume with the same solution. After mixing, an aliquot was transferred to a transmission cell and the absorbance read at 470 millimicrons and at 570 millimicrons.

The amount of iron was calculated* using specific extinction coefficient values from the standard curves, (Fig.7) at 470 and 570 millimicrons.

(d) Determination of Aluminum.

The process of extraction was the same as that for iron, except the aluminum was extracted from an aliquot added to 25 mls. of 4% sodium acetate solution at a pH equal to 5.8. The absorbance was read at 387.5 millimicrons for aluminum and at 570 millimicrons for iron.

* Sample calculation.

Absorbance at 470 millimicrons = 0.696

From figure 7, concentration in grams $\times 10^{-6}$ /ml.

$$= 9.83 \times \text{Absorbance},$$

where specific extinction coefficient = $\frac{1}{9.83}$ for iron at 470 millimicrons.

Aliquot volume = 5 mls.

Amount of iron in sample = $0.696 \times 9.83 \times \frac{100 \times 10}{5}$

$$= 1370 \times 10^{-6} \text{ grams.}$$

Amount of iron determined in blank = 290×10^{-6} grams.

Therefore, amount of iron per 20 grams of rubber sample

$$= 1080 \times 10^{-6} \text{ grams.}$$

The concentration of the iron in the chloroform extract was obtained from the preceding calculations for iron, and the absorbance due to this amount of iron was obtained from the standard curve for iron at 387.5 millimicrons (Fig.7). This absorbance was subtracted from the absorbance of the sample at 387.5 millimicrons. The amount of aluminum was calculated* from the net absorbance using the standard curve (Fig.7).

* Sample calculation.

Amount of iron in solution = 1380×10^{-6} grams.

Dilution volume = 100 mls.

Aliquot volume = 0.5 mls.

Amount of iron in aliquot = $1380 \times \frac{0.5}{100 \times 10} = 0.690 \times 10^{-6}$ gms/ml.

From figure 7, the absorbance produced at 387.5 millimicrons by

$$0.690 \times 10^{-6} \text{ grams of iron/ml.} = 0.059$$

Absorbance for sample = 0.277

Absorbance by aluminum in sample solution = $0.277 - 0.059 = 0.218$.

From figure 7 -- concentration in grams $\times 10^{-6} = 4.04 \times$ Absorbance, where $\frac{1}{4.04}$ = specific extinction coefficient for aluminum at

387.5 millimicrons.

Amount of aluminum in sample = $0.218 \times 4.04 \times \frac{100 \times 10}{0.5}$

$$= 1760 \times 10^{-6} \text{ grams}$$

Similarly, amount aluminum in blank = 60×10^{-6} grams.

Therefore, amount of aluminum per 20 grams of rubber sample

$$\begin{aligned} &= 1700 \times 10^{-6} \text{ grams} \\ &= 0.0017 \text{ grams.} \end{aligned}$$

(e) Separation of Nickel and Copper.

The procedure is the one outlined by Sandell (19).

The ammoniacal filtrate from the iron and aluminum separation procedure was almost neutralized with hydrochloric acid, then 5 drops of concentrated ammonia hydroxide were added.

To this solution was added 40 drops of 2% solution of dimethyl glyoxime in ethanol. The mixture then was extracted three times with 3 ml. portions of chloroform in a separatory funnel. The chloroform extract was transferred to another separatory funnel, and the aqueous solution containing the copper transferred to a volumetric flask. The combined extracts then were shaken with a 10 ml. portion of 0.1N ammonium hydroxide for one minute, and the chloroform portion run into a third separatory funnel. The water layer was shaken for one minute with a 3 ml. portion of chloroform and the chloroform extracts combined. The water layer was added to the flask containing the copper solution.

(f) Determination of Nickel.

The chloroform solution containing the nickel was shaken successively with two 5 ml. portions of 0.5 N hydrochloric acid. Acid extracts were transferred to a 25 ml. volumetric flask. Two drops of concentrated hydrochloric acid were added, then 5 drops of saturated bromine water. The solution then was allowed to stand for half an hour. To the brominated solution concentrated ammonium hydroxide was added until the bromine color disappeared, then 5 drops were added in excess. Then 20 drops of 2 % dimethyl glyoxime solution were added, the mixture diluted to 25 ml. with

water and mixed. An aliquot was quickly transferred to a transmission cell, and the absorbance measured at 460 millimicrons.

The amount of nickel was determined from the standard curve in figure 8. Calculations for nickel are the same in method as those for iron.

(g) Determination of Copper.

The extraction procedure is the same as that for iron. The buffer solution used was a 4 % ammonium tartrate solution. If the aliquot to be used was over 25 mls., solid ammonium tartrate was added to the aliquot to produce a 4 % solution. Absorbances were read at 410 millimicrons, and the copper content calculated using the standard curve, (Fig.9). Calculations for copper are the same in method as those for iron.

3. RESULTS AND DISCUSSION OF RESULTS.

A. DETERMINATION OF ASH CONTENT AND SILICA.

The amounts of ash, silica and total insoluble residue obtained from 20 gram samples of rubber are tabulated in Table 4.

It would appear from Table 4, that all the samples contain some silica and that natural rubber contains appreciably more than any of the other types of rubber.

There would appear to be no measurable amount of "total insoluble residue" in the natural, Polysar Krylene, and Polysar S samples. The residues from the Polysar Krynac and the Polysar Butyl samples were treated with hot concentrated sulphuric acid and with ammonium acetate in an attempt to identify them. Since the insoluble residue did not dissolve to any extent in the hot ^{con}centrated sulphuric, it would seem that there was no barium sulphate. In addition, the filtrate from the acid treatment gave no tests for barium, when tested with potassium chromate and by means of a flame. Similarly, the filtrate from the ammonium

Footnotes to Table 4.

- (a) The ash content was the residue from the 8-quinolate precipitation process after ignition. (see page 23)
- (b) This is the residue obtained after digestion with perchloric acid and filtration. (see page 24)
- (c) The total insoluble residue is the sum of two hydrochloric acid insoluble residues ; the acid insoluble residue obtained after the removal of the silica, (see page 24), and the acid insoluble residue obtained after redissolving the hydroxides of aluminum and iron. (see page 25).

CHAPTER XXV. — THE REVOLUTIONARY PERIOD.
1774-1780.

THE first of the revolutionary period was the year 1774, when the British evacuated Boston and the Continental Congress fled to Lancaster and then to York. The city was then under the control of the British, who remained until 1776. During this time, the city suffered from a severe winter and a lack of food and shelter. The British also imposed a strict curfew and a ban on public gatherings. Despite these hardships, the city's residents remained loyal to the Continental Congress and the revolutionary cause. In 1776, the British evacuated Boston and the Continental Congress moved back to the city. The city then became a center of revolutionary activity, with many of the city's residents serving in the Continental Army. The city's role in the revolution was significant, and it played a key role in the establishment of the new nation.

CHAPTER XXVI. — THE REVOLUTIONARY PERIOD.
1780-1785.

THE second of the revolutionary period was the year 1780, when the British evacuated Boston and the Continental Congress fled to Lancaster and then to York. The city was then under the control of the British, who remained until 1780. During this time, the city suffered from a severe winter and a lack of food and shelter. The British also imposed a strict curfew and a ban on public gatherings. Despite these hardships, the city's residents remained loyal to the Continental Congress and the revolutionary cause. In 1780, the British evacuated Boston and the Continental Congress moved back to the city. The city then became a center of revolutionary activity, with many of the city's residents serving in the Continental Army. The city's role in the revolution was significant, and it played a key role in the establishment of the new nation.

Table 4. Weights of Ash, Silica and Total Insoluble Residue

Obtained from Twenty grams of Various Rubber Samples.

Sample .	Sample Number .	Ash ^a Content .	Perchloric ^b Acid Residue .	Silica .	Total ^c Insoluble Residue .
		grams .	grams .	grams .	grams .
Natural Rubber	1	0.0477			
	6	0.0417		0.0260	
	7	0.0416	0.0322	0.0211	
	31	0.0525	0.364	0.0324	0.0007
	32	0.0536	0.0424	0.0388	0.0006
	33	0.1022	0.0831	0.0785	0.0006
Blank	34	0.0050	0.0041	0.0027	0.0006
Polysar Krylene	3	0.0414			
	11	0.0369		0.0084	
	12	0.0475	0.0342	0.0113	
	35	0.0243	0.0080	0.0048	0.0008
	36	0.0304	0.0095	0.0061	0.0010
	37	0.0241	0.0033	0.0026	0.0008
Blank	38	0.0039	0.0014	0.0007	0.0008
Polysar S.	2	0.0312			
	21	0.0440		0.0031	
	22	0.0364	0.0337	0.0099	
	39	0.0312	0.0104	0.0062	0.0006
	40	0.0294	0.0043	0.0039	0.0006
	41	0.0299	0.0046	0.0038	0.0006
Blank	42	0.0036	0.0008	0.0007	0.0006
Polysar Krynac	4	0.0792			
	16	0.0584		0.0019	
	17	0.0223	0.0077	0.0026	
	43	0.0657	0.0027	0.0018	0.0058
	44	0.0666	0.0032	0.0022	0.0057
	45	0.0647	0.0050	0.0029	0.0091
	46	0.0666	0.0035	0.0022	0.0085
Blank	47	0.0036	0.0008	0.0004	0.0011
Polysar Butyl	5	0.0555			
	26	0.0660		0.0055	
	27	0.0779	0.0120	0.0052	
	48	0.0720	0.0390	0.0061	0.0333
	49	0.0826	0.0379	0.0017	0.0336
	50	0.0754	0.0332	0.0025	0.0360
Blank	51	0.0030	0.0007	0.0007	0.0004

acetate treatment gave no reactions with potassium chromate or potassium iodide. These tests, along with the fact that the residue did not dissolve to any extent in ammonium acetate, would indicate that lead sulphate was absent. Other simple tests failed to provide positive identification of this total insoluble residue. To identify this material, it would seem as though a spectrographic examination of this residue is necessary.

B. DETERMINATION OF IRON.

The experimental data relative to the determination of iron in the rubber samples is listed in Tables 5 and 6.

The results indicate that the rubber samples are relatively uniform in iron content. It is obvious however that there are variations among samples taken from the same type of rubber. It is therefore likely that these types of rubbers are not homogeneous as far as inorganic material is concerned.

A comparison of the values obtained for iron at 470 millimicrons and at 570 millimicrons, (see columns 6 and 9, Table 5; column 6, Table 6), is evidence that the absorbance measurements and extraction procedures are reliable. No measurements were made for iron in Polysar Krynac, Table 6, since the aliquots taken were too small to provide reliable figures.

C. DETERMINATION OF ALUMINUM.

The experimental data relative to the determination of aluminum in various rubber samples is listed in Table 7.

The amounts of aluminum determined in the Polysar Krynac samples are much higher than in any other rubber samples. Though natural rubber has an intermediate and probably variable aluminum

Table 5. Amounts of Iron as Determined from Twenty gram Samples of Rubber. Extraction was made from an Ammonium Tartrate Buffer Solution.

Sample	Sample Number	Aliquot taken from 100 mls. of solution	Absorbance at 470 mμ.	Total Iron $\times 10^6$	Iron ^a Corrected $\times 10^6$	Absorbance at 570 mμ.	Total Iron $\times 10^6$	Iron Corrected $\times 10^6$
Natural Rubber.	31	5.0 ml.	0.696	1370	1080	0.463	1380	1080
	32	5.0 ml.	0.463	1670	1380	0.570	1680	1390
	33	5.0 ml.	1.449	2850	2570	0.962	2860	2560
Blank.	34	5.0 ml.		291		0.100	300	
Polysar	35	2.0 ml.	0.641	3150	2920	0.428	3180	2950
Krylene.	36	2.0 ml.	0.755	3710	3480	0.504	3720	2490
	37	2.0 ml.	0.115	566	338	0.075	557	331
Blank.	38	5.0 ml.	0.116	228		0.078	236	
Polysar S.	39	2.0 ml.	0.501	2470	2290	0.334	2480	2300
	40	5.0 ml.	0.669	658	481	0.445	662	482
	41	5.0 ml.	0.829	815	538	0.555	824	644
Blank.	42	5.0 ml.	0.180	177		0.121	180	
Polysar Krynac.	43	5.0 ml.	0.691	1360	1190	0.459	1360	1190
	44	5.0 ml.	0.752	1480	1310	0.501	1490	1320
	45	5.0 ml.	0.600	1180	1010	0.407	1210	1040
	46	5.0 ml.	0.651	1280	1110	0.431	1280	1110
Blank.	47	10.0 ml.	0.170	169		0.115	171	
Polysar Butyl.	48	10.0 ml.	0.296	291	126	0.200	297	128
	49	10.0 ml.	0.315	310	145	0.210	312	143
	50	10.0 ml.	0.331	325	160	0.225	334	165
Blank.	51	10.0 ml.	0.168	165		0.114	169	

^a See page 26, sample calculation.

Table 6. Amounts of Iron as Determined from Twenty grams of Rubber. Extraction was made from an Acetate Buffer Solution.

Sample	Sample Number	Aliquot taken from 100 mls. solution	Absorbance at 570 mp.	Total Iron gms. x 10 ⁶	Iron ^a Corrected gms. x 10 ⁶
Natural Rubber	31	0.5 ml.	0.047	1400	1100
	32	0.5 ml.	0.060	1780	1490
	33	0.5 ml.	0.099	2940	2650
Blank	34	5.0 ml.	0.099	294	
Polysar	35	0.5 ml.	0.109	3240	2990
Krylene	36	0.5 ml.	0.125	3720	3470
	37	1.0 ml.	0.040	594	345
Blank	38	5.0 ml.	0.084	249	
Polysar	39	0.5 ml.	0.086	2560	2370
S.	40	1.0 ml.	0.052	773	585
	41	2.0 ml.	0.122	906	718
Blank	42	5.0 ml.	0.063	188	
Polysar	48	0.5 ml.	0.098	291	127
Butyl	49	2.0 ml.	0.040	297	133
	50	2.0 ml.	0.042	312	148
Blank	51	5.0 ml.	0.055	164	

^a See page 26, sample calculation.

Table 7. Amounts of Aluminum in Twenty gram Samples of Rubber. Extraction was made from an Acetate

Buffer Solution.

Sample	Sample Number	Aliquot taken from a 100 ml. solution	Total ^a Iron gms. x 10 ⁶	Absorbance due to Iron at 387.5 mμ.	Absorbance Sample Solution at 387.5 mμ.	Net Absorbance Aluminum	Amount Aluminum gms. x 10 ⁶	Aluminum ^b Corrected gms. x 10 ⁶
Natural Rubber	31	0.5 ml.	1380	0.059	0.277	0.218	1760	1700
	32	0.5 ml.	1710	0.073	0.320	0.247	2000	1940
	33	0.5 ml.	2880	0.123	0.640	0.517	4180	4120
	34	5.0 ml.	294	0.126	0.197	0.071	57	
Polysar Krylene	35	0.5 ml.	3190	0.136	0.146	0.010	81	18
	36	0.5 ml.	3770	0.159	0.170	0.011	89	26
	37	1.0 ml.	572	0.049	0.071	0.022	89	26
	38	5.0 ml.	234	0.143	0.222	0.079	63	
Polysar S.	39	0.5 ml.	2500	0.107	0.126	0.019	156	107
	40	1.0 ml.	698	0.060	0.093	0.033	132	83
	41	2.0 ml.	848	0.145	0.214	0.069	139	90
	42	5.0 ml.	182	0.078	0.138	0.060	49	
Polysar Krynac	43	0.2 ml.	1360	0.023	0.825	0.802	16,200	16,200
	44	0.2 ml.	1480	0.025	0.873	0.848	17,100	17,100
	45	0.2 ml.	1200	0.020	0.823	0.803	16,200	16,200
	46	0.2 ml.	1280	0.022	0.852	0.830	16,800	16,700
Blank	47	5.0 ml.	171	0.073	0.124	0.051	41	
								16,700
Polysar Butyl	48	0.5 ml.	293	0.012	0.630	0.618	489	458
	49	2.0 ml.	306	0.052	0.266	0.214	432	401
	50	2.0 ml.	324	0.055	0.285	0.230	464	433
	51	5.0 ml.	166	0.071	0.109	0.138	31	

^a The iron values are the average of the amounts given in Table 5.^b See sample calculation, page 27.

content, the other rubber samples are all relatively low in aluminum.

D. DETERMINATION OF NICKEL.

The experimental data relative to the determination of the amounts of nickel in the various rubber samples is listed in Table 8.

Unfortunately, there appeared to be more nickel in the reagents used than there was in the samples under examination. Therefore, the amounts found can only be reported as less than the amounts found in the blank for that series. The high value in sample number 41 was probably due to an accidental contamination through the unfortunate use of nickel tongs during the separation procedure.

E. DETERMINATION OF COPPER.

The experimental data relative to the determination of the amounts of copper in various rubber samples is listed in Table 9.

Amounts of copper found in the various samples are about the same, though natural rubber samples appear to contain slightly more copper than the other samples. The value for copper in sample number 41 is probably an error due to the incomplete removal of the nickel from the copper.

Table 8. Amounts of Nickel in Twenty gram Samples of Rubber.

Sample	Sample Number	Absorbance at 460 mμ.	Nickel in Solution gms. x 10 ⁶	Nickel Corrected gms. x 10 ⁶
Natural Rubber	31	0.242	23.4	0.1
	32	0.317	30.6	7.3
	33	0.309	29.8	6.5
Blank	34	0.241	23.3	
Polysar	35	0.217	20.9	8.5
Krylene	36	0.170	16.4	4.0
	37	0.210	20.3	8.0
Blank	38	0.128	12.4	
Polysar	39	0.179	17.3	2.1
S.	40	0.163	15.7	.5
	41	high		
Blank	42	0.158	15.2	
Polysar	43	0.194	18.7	4.3
Krynac	44	0.169	16.3	1.9
	45	0.117	11.3	
	46	0.248	23.9	9.5
Blank	47	0.149	14.4	
Polysar	48	0.407	39.2	5.7
Butyl	49	0.202	19.5	6.0
	50	0.148	14.3	.8
Blank	51	0.140	13.5	

Nickel corrected equals nickel in solution minus nickel in blank

Table 9. Amounts of Copper in Twenty gram Samples of Rubber

Sample	Sample Number	Aliquot Taken From a 100 ml. solution	Absorbance at 410 mp.	Copper in Solution gms. x 10^6	Copper Corrected gms. x 10^6
Natural Rubber	31	100	1.123	132	69
	32	100	1.446	169	106
	33	25	0.308	144	81
Blank	34	100	0.538	63	
Polysar	35	25	0.214	100	42
Krylene	36	25	0.175	82	24
	37	25	0.298	139	81
Blank	38	100	0.499	58	
Polysar	39	100	0.835	98	38
S	40	100	0.648	76	16
	41	25	1.095	514	high
Blank	42	25	0.128	60	
Polysar	43	100	1.003	118	64
Krynac	44	100	0.599	70	16
	45	100	0.492	57	3
	46	25	0.159	74	20
Blank	47	100	0.461	54	
Polysar	48	25	0.164	77	24
Butyl	49	25	0.197	92	39
	50	25	0.219	103	50
Blank	51	100	0.454	53	

copper corrected equals copper in solution minus copper in blank.

4. SUMMARY OF RESULTS.

Spectrographic examination has indicated that aluminum, barium, calcium, copper, iron, lead, magnesium, nickel, silica, silver, tin, titanium, and zinc are present in all samples of rubber examined. Chemical analysis was carried out for aluminum, copper, iron, nickel and silica, the experimental data of Tables 4 to 9 being summarized in Table 10, on the following page. Agreement among different samples from the same type of rubber is poor. If the analytical procedures were adequate, this would indicate that the samples are not homogeneous in their composition. Since the amounts of reagents added to any one series of samples were the same in all cases, the blanks are a good indication of the impurities in the reagents. It was not realized that the blanks would be so high, especially in copper and nickel. The major cause of the high blank values obtained was undoubtedly due to the large amounts of acids that were used to decompose the rubber. The average values of Table 10 are given in Table 11.

Spectrophotometric analysis of the metal 8-quinolate complexes in chloroform was found to be very satisfactory for the analysis of aluminum, copper and iron.

The variability of the values obtained for a series of determinations, (see Table 10), would indicate the samples are not homogeneous. The inorganic constituents are possibly the result of accidental contamination.

Table 10. Summary of the Analyses of the Inorganic Components in the Various Rubber Samples.

Sample	Sample Number	% Ash	% Silica	% Total Insoluble Residue	% Iron $\times 10^{+4}$	% Aluminum $\times 10^{+4}$	% Copper $\times 10^{+6}$	% Nickel $\times 10^{+6}$
Natural Rubber	31	0.238	0.148	<0.0005	54.4	85.0	345.	<120
	32	0.243	0.180	<0.0005	71.0	87.0	530.	<120
	33	0.486	0.379	<0.0005	130.	206.	400.	<120
Polysar Krylene	35	0.102	0.020	<0.0005	148.	<3.0	<290	<60
	36	0.132	0.027	<0.0005	157.	<3.0	<290	<60
	37	0.101	0.010	<0.0005	16.9	<3.0	<290	<60
Polysar S.	39	0.138	0.028	<0.0005	116.	5.4	<300	<76
	40	0.129	0.016	<0.0005	25.8	4.1	<300	<76
	41	0.132	0.012	<0.0005	31.6	4.5	<300	<76
Polysar Krynac	43	0.310	0.007	0.024	58.5	810.	<270	<72
	44	0.315	0.009	0.023	65.2	855.	<270	<72
	45	0.310	0.012	0.040	51.2	810.	<270	<72
	46	0.315	0.009	0.037	55.6	835.	<270	<72
Polysar Butyl	48	0.348	0.027	0.164	5.2	27.9	<260	<70
	49	0.398	0.005	0.166	7.0	20.0	<260	<70
	50	0.362	0.009	0.178	7.9	21.6	<260	<70

Table 11. The Average Values for the Analyses of the
Various Rubber Samples.

Sample	% Ash	% Silica	% Insoluble Residue	% Iron	% Aluminum	% Copper	% Nickel
Natural Rubber	0.32	0.27	<0.0005	0.008	0.013	0.0004	<0.0001
Polysar Krylene	0.112	0.019	<0.0005	0.01	<0.0003	<0.0003	<0.0001
Polysar S.	0.133	0.019	<0.0005	0.006	0.0005	<0.0003	<0.0001
Polysar Krynac	0.312	0.009	0.031	0.0058	0.083	<0.0003	<0.0001
Polysar Butyl	0.37	0.017	0.169	0.0007	0.0023	<0.0003	<0.0001

5. BIBLIOGRAPHY

1. American Society for Testing Materials, Part 6, 1952.
2. Bekkedahl N. Anal. Chem. 25, 54-64, (1953).
3. Genty C.H.R. and Sherrington L.G. The Analyst 75, 17, (1950).
4. Gunn E. and Po ers J.M. Anal. Chem. 24, 742-6, (1952).
5. Hamlin A.G. Journal of the Textile Institute. 40, 343-55, (1949).
6. Harris E.M. Chem. Eng. 56, 148-51, (1949).
7. Heggen G.E. and Strock L.W. Anal. Chem. 25, 859-63, (1953).
8. Kahane E. Ann. chim. anal. chim. appl. 2, 261-4, (1927).
9. Karcher J.H. and Gunn E. Anal. Chem. 24, 1733-41, (1952).
10. Key C.W. and Hoggan G.D. Anal. Chem. 25, 1673-6, (1953).
11. Meeker R.F. and Pomatti R.C. Anal. Chem. 25, 151-4, (1953).
12. Milner O.J. and co-workers. Anal. Chem. 24, 1728-32, (1952).
13. Mitteldorf A.J. and Landon D.O. Anal. Chem. 24, 469-72, (1952).
14. Moeller T.J. Ind. and Eng. Chem. Anal. Ed. 15, 346, (1943).
15. Morgan L.O. and Turner E.S. Anal. Chem. 23, 978, (1951).
16. Rabald A.C. Rubber Age 71, 621-24, (1952).
17. Rees W.T. The Analyst 75, 160, (1950).
18. Sandell E.B. Colorimetric Determination of Trace Metals,
Interscience Publishers, New York, 1944.
19. Ibid. Page 339.

B29769